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(71) Applicant *(for all designated States except US)*: F.LLI ZUCCHINI S.R.L. [IT/IT]; Via C. Colombo, 6, I-44044 Ferrara-Cassana (IT).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: CALDARI, Graziano [IT/IT]; Via Resistenza, 28, I-44044 Ferrara (IT). BRIGHENTI, Alberto [IT/IT]; Via Aldo Chiorboli, 193, I-44044 Ferrara (IT).

(74) Agent: DALL'OLIO, Giancarlo; Interbrevetti S.r.l., Via del Cestello, 13, I-40124 Bologna (IT).

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(54) Title: METHOD FOR BONDING PLASTIC MATERIALS

(57) Abstract

The method for bonding polyolefin plastic materials, omopolymers, copolymers, either thermoplastic or cross-linked, expanded or not expanded, alone or properly compounded with plasticizers, extender, fillers, mineral or organic fibres, stabilizers, chemical additives, includes the application of a coat of a solution containing 0.5 % up to 10 % of a chlorinated organic compound dissolved into an organic solvent, blend in the ratio of 99.5 % to 90 %; a first evaporation of solvents contained in the solution; the exposure of the surface treated with the solution to ultraviolet radiations; the subsequent cooling; the application of an adhesive in solution of organic solvents or in water dispersion onto the polyolefin plastic material prepared as above and onto another material to be bonded thereto, followed by a second evaporation of organic solvents contained in the adhesive, or the application of melted non volatile adhesive onto the polyolefin plastic material and onto another material to be bonded thereto; the coupling of said materials applying pressure.

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METHOD FOR BONDING PLASTIC MATERIALS

TECHNICAL FIELD

The present invention concerns the bonding of plastics, particularly relates to a method for bonding polyolefins.

BACKGROUND ART

It is known that it is relatively difficult to bond plastics such as polyolefins, omopolymers, copolymers, either thermoplastic or crosslinked, expanded or not expanded, alone or properly compounded with plasticizers, extender, fillers, organic or inorganic fibres, stabilizers, chemical additives, to other organic and inorganic, natural or synthetic materials, such as leather, hide, polyvinylchloride and polyurethane, metal, concrete, ceramics. The principal reason of such a weak and unsufficient bond comes from the low polarity and surface energy of these kind of plastic materials, especially when the bond is carried out with traditional adhesive systems.

Moreover, it is known that the bond of the above mentioned polyolefins, can be improved subjecting their surfaces to chemical and physical treatments fit to increase their surface energy and polarity. Normally this is reached by using technics such as the corona-discharge treatment, plasma treatment, exposure to ultraviolet radiations, flame treatment, surface chemical grafting.

Nevertheless, these surface treatments are not sufficient or not suitable in practice, when a very high bond resistance is required, similar in value to the cohesion of the bonded materials, for example in bonding shoe components, such as soles or midsoles, in bonding waterproofing or fluid-tight membranes, slabs for wall-paneling or for flooring, or insulating panels, fluid transport piping, to substrates of different nature as metal, concrete, plastics, ceramics, or in structural bonding on rigid or semirigid plastic structures in several industrial applications.

It is to be emphasized that it is practically impossible to implement flame treatments in a shoe factory due to safety reasons. Most of the shoes are realized with soles of synthetic materials including, for example, styrenebutadiene rubber, styrene-butadiene-styrene o

styrene-isoprene-styrene rubbers, ethylenevinylacetate, polyurethane, polyvinylchloride, polyolefins.

For example the known methods for bonding soles to natural or synthetic uppers, for example with polyurethane adhesives, involve a previous treatment of the soles with a specific solution of a chlorine donor compound and then, after the application of the polyurethane adhesive onto both the soles and the uppers, the assembly of the parts under pressure.

The main disadvantage of the known methods is that very often the bond obtained does not satisfy the requirements of the bond itself. In fact in the case of soles or midsoles made with polyolefins, omopolymers, copolymers, either thermoplastic or crosslinked, expanded or not expanded, based on polypropylene, polyethylene, ethylenevinylacetate, the bond values reached with the known methods are very low and not sufficient.

Further disadvantage of such a known methods is the resulting chlorine emission which is noxius for the environment.

The known methods for bonding polyolefins in fields other than footwear, include a previous chemical and physical treatments fit to increase their surface energy and polarity. Normally this is reached by using technics such as the corona-discharge treatment, plasma treatment, exposure to ultraviolet radiations, flame treatment, surface chemical grafting.

Each method then involves the subsequent application of an adhesive, more frequently of a paint to polyolefins so treated.

Besides the mentioned methods, it is known that polyolefins can be bonded also by applying a primer based on polychloroolefins dissolved in organic solvents that, after drying, leaves a polar film that makes the surface fit to receive the subsequent application of polychloroprene or polyurethane adhesives, more frequently than paints.

The main disadvantage of these known methods is that, although in painting operations they could be useful for obtaining a good and durable adhesion of the paint film,

howewer in bonding polyolefin plastic materials, often they do not meet the requirements of the whished bonding.

DISCLOSURE OF THE INVENTION

The main aim of the present invention is to provide a bonding method fit to improve, compared with the known art, the bond value obtainable on polyolefinic plastic materials, omopolymers, copolymers, either thermoplastic or crosslinked, expanded or not, alone or properly compounded with plasticizers, extender, fillers, mineral or organic fibres, stabilizers, chemical additives.

Further aim of the present invention is to provide a bonding method and a usage of adhesive compositions that, when implemented, are such as to release insignificant chlorine amounts to the einvironment.

The aims as above are achieved according to the content of the claims.

BEST MODE OF CARRYING OUT THE INVENTION

Each used surface is made by polyolefinic plastic materials, omopolymers, copolymers, either thermoplastic or crosslinked, expanded or not expanded, alone or properly compounded with plasticizers, extender, fillers, mineral or organic fibres, stabilizers, chemical additives. For ease of reference each of such surfaces shall be henceforth called SURFACE S.

Plastic materials are mainly shoe components, e.g. soles and midsoles, waterproofing or fluid-tight membranes, slabs for wall-paneling or for flooring, insulating panels and rigid or semirigid plastics structures, fluid transport pipes.

These materials, especially waterproofing and fluid-tight membranes, slabs for wall-paneling or for flooring, insulating panels and rigid or semirigid plastics structures, pipes, are bonded with each other or with substrates of different nature, such as metals, concrete, plastics or ceramics.

The method for bonding polyolefins basically includes the following steps:

- the application onto each SURFACE S of a coat of a solution containing 0.5% up to 10% of a chlorinated organic compound dissolved into an organic solvent blend in the ratio of 99.5% to 90 %;
- a first evaporation of solvents contained in said solution;
- the exposure to ultraviolet radiations of the SURFACE S treated with said solution;
- the cooling of the SURFACE S;
- the application of an adhesive, in solution of organic solvents or in water dispersion, with or without crosslinker, both onto the SURFACE S and the surface of another substrate to which said SURFACE S has to be bonded, this application being followed by a second evaporation of the organic solvents or water contained in the adhesive, or the application of a melted 100% not volatile adhesive both onto the SURFACE S and the other material to be bonded thereto:
- the coupling , applying pressure, of the treated surfaces of said materials.

The application of the adhesive to the SURFACE S it coul be followed by a heat reactivation of the treated surfaces of said SURFACE S to be bonded together.

The method may also include solvent cleaning of the SURFACES S, this being often required for removing from these surfaces release agents or contaminants which may be onto it, the cleaning is carried out by using a solvent belonging to the group of ketone, or esters, or chlorinated, aromatics or aliphatics hydrocarbons, such as methyl ethyl ketone, acetone, ethyl acetate, trichloroethylene, toluene, or their blends.

The composition, henceforth referred to as PRIMER, of the preferred embodiment, includes organic compounds based on chlorinated natural rubber, e.g. of the Pergut S20 (Bayer trademark) or Alloprene (ICI trademark) and formulated as follows:
-chlorinated natural rubber in the ratio of 0.5% up to 10%;
-organic solvent blend in the ratio of 99.5% to 90%.

The solvent blend contains solvent such as toluene, methyl ethyl ketone, ethyl acetate, acetone and other organic solvents in various proportions, as necessary to dissolve the chlorinated natural rubber. A favorite blend is the following::

- toluene	10%
- methyl ethyl ketone	20%

- ethyl acetate 35%
- acetone 35%

In the PRIMER, the chlorinated natural rubber can be replaced by vinylchloroacetate resins, e.g. Vinylite VMCH (trademark of the Union Carbide Chemicals), or by chlorinated polyethylene, e.g. Hypalon (trademark of Du Pont Dow Elastomers), by acrylic polymers and copolymers, e.g. chlorovinylacrylic resin like Haloflex (marchio della ZENECA Resins), by polychloroprene polymers, e.g Neoprene (marchio DuPont Dow Elastomers) and by phenolic resins.

The application of a very thin layer of PRIMER to the area of SURFACE S to be subsequently bonded is made by means of a brush or of a spreading machine or roller spreader, or by a spray equipment.

The first evaporation or drying of solvents contained in the solution takes a few minutes, preferably 5 to 6 minutes.

The source of ultraviolet radiations is a ultraviolet rays lamp having, for example, the following characteristics: a high to medium vapour pressure mercury light having total power ranging from 400 to 4000 Watt.

For example it is preferable to use a tube 35 cm long having a power of 100 Watt/cm. Such a lamp can emit the complete range of ultraviolet wavelenghts from 184nm to 366nm, this with different strenghts but with prevailing presence of wavelenghts included from 210nm to 336nm, and significant presence of wavelenghts included from 210nm to 254nm.

The exposition to the ultraviolet radiation lamp of the SURFACE S area treated with the PRIMER for a time from 5 up to 30 seconds depending on the condition in which the distance of the radiation source from the SURFACE S can vary from 0.1 to 0.3 metres.

The adhesive is, for example, based on polymers such as polyurethane, polycloroprene, styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS) block copolymers, styrene-butadiene rubber, nitrile rubber, acrylic resins, cyanoacrylate, vinyl resins, epoxy

resins dissolved in a blend of organic solvents, or in water dispersion, or in a 100% non volatile composition, with or without curing agent.

The application of said adhesive to SURFACE S takes place after cooling of this surface.

Having allowed a second drying time as necessary for evaporation of solvents contained in the adhesive, then the adhesive films coated onto the surfaces are reactivated at a temperature ranging from 20°C to 80 °C.

Finally, adhesive coated areas of SURFACE S can be positioned and assembled to the other surface, and then a pressure which can indicatively range from 3 to 5 bar, is applied to the assembly.

It is to point out that second evaporation does not take place when the adhesive composition is 100% non volatile and that heat-reactivation is not always required with this kind of adhesives, or anyway when the adhesive at room temperature has a tackiness sufficient to carry out the bond, as the most polychoroprene adhesives.

It follows examples concerning different formulation of the PRIMER solution.

EXAMPLE 1.0: a chlorinated natural rubber, e.g. Pergut (Bayer AG trademark) preferably having viscosity of 20 mPa.s at 20°C in 20% toluene, such as Pergut S20 (trademark of Bayer AG), is dissolved in a blend of organic solvents preferably as follows:

PRIMER 1

Pergut S20 (Bayer AG trademark)	2,16
toluene	10,29
methyl ethyl ketone	18,47
ethyl acetate	34,88
acetone	34,20
TOTAL	100,00

The method of the present invention, using the above mentioned PRIMER, is hereafter disclosed and called PROCESS P.0.

This solution is applied to the SURFACE S of ethylenevinylacetate, crosslinked and expanded, wiped with methyl ethyl ketone for removing from the surface the release agents used in moulding process.

After 2 to 5 minutes drying time the SURFACE S is exposed to UV rays preferably passing the same through an oven provided in its upper side with ultraviolet rays tubular lamps 35 cm long and 100 Watt/cm power, set with a reflecting shelter fit to focus up to a certain extent the rays to an area of above 20 centimetres distant from the lamp. At such distance the SURFACE S is transported onto a conveyor so that to be treated inside the oven. Dwelt time in the oven is about 30 seconds, though the effective dwell time in the focus area is about 5 to 12 seconds.

Then SURFACE S is allowed to cool for a few minutes, about 5 minutes, and next bonded to PVC with a polyurethane heat reactivable adhesive, for example by using EN1392 standard method.

Bond values (Kg/cm) achieved with PROCESS P.0 by using PRIMER 1 are shown in the following TABLE 1.0.

The SURFACES S of ethylenevinylacetate will be hereinafter referred to as EVA, the ones of polypropylene as PP, and the ones of low density polyethylene as PE LD.

"Initial strenght" means here the resistance of the adhesive to peel taken immediately after pressing of parts as described in EN1392 standard method. Such a resistance is expressed in Kg/cm.

TABLE 1.0

SURFACE S	Initial strenght	type of failure	Final streng	type of failure
EVA not expanded	2-3	adhesion	5-6	adhes./cohesion EVA
EVA expanded	2-3	adhesion	5-6	adhes./cohesion EVA
PP *	3-5	adhesion	5-9	adhes./cohes. on surface
PE LD *	3-7	adhesion	9-15	adhes./cohes. on surface

* wiped con Nappar6 (EXXON trademark)

EXAMPLE 1.1: Process P.1: the composition PRIMER 1 is applied on SURFACE S of polypropylene wiped with methyl ethyl ketone for removing from surface the release agents used in moulding process.

After 2 to 5 minutes drying time SURFACE S is exposed to UV rays preferably letting the same through an oven provided in its upper side with ultraviolet rays tubular lamps 35 cm long and 100 Watt/cm power, set with a reflecting shelter able to focus up to a certain extent the rays to an area of about 20 cm distant from the lamp. At such distance SURFACE S is conveyed on a belt so that to be treated inside the oven. Dwell time in the oven is about 30 seconds, though the effective dwell time in the focus area is about 5 to 12 seconds.

Then SURFACE S is allowed to cool for a few minutes, about 5 minutes, and next bonded to previous abraded leather, by using solvent based or water based adhesives.
Bond values Kg/cm obtained with PROCESS P.1 by using PRIMER 1 are shown in the following TABLE 1.1.

TABLE 1.1 bond on leather (peel values at 72 hours from the bond following EN 1392, Kg/cm)

SURFACE S= PP*	Final strenght	type of failure
acrylic adhesive in water dispersion	5-6	leather cohesion
nitrile adhesive in organic solvent blend	5-6	leather cohesion
polychloroprene adhesive in organic solvent blend	5-6	leather cohesion
SBS adhesive in organic solvent blend	5-6	cohes.of adhesive /leather
vinyl adhesive in water dispersion	5	leather cohesion

* wiped with methyl ethyl ketone

EXAMPLE 1.2: Process P.2: the composition PRIMER 1 is applied on SURFACE S of polypropylene wiped with methyl ethyl ketone for removing from surface the release agents used in moulding process.

After 2 to 5 minutes drying time SURFACE S is exposed to UV rays preferably letting the same through an oven provided in its upper side with ultraviolet rays tubular lamps 35 cm long and 100 Watt/cm power, set with a reflecting shelter able to focus up to a certain extent the rays to an area of about 20 cm distant from the lamp. At such distance SURFACE S is conveyed on a belt so that to be treated inside the oven. Dwel time in the

oven is about 30 seconds, though the effective dwell time in the focus area is about 5 to 12 seconds.

Then SURFACE S is allowed to cool for a few minutes, about 5 minutes, and next bonded to wood by using solvent based or water based adhesives or a 100% non volatile adhesive in melted phase.

Bond values obtained with PROCESS P.2 by using PRIMER 1 are shown in the following TABLE 1.2.

TABLE 1.2: bond to wood (shear strenght as Kg/cm^2 following UNI-EN205)

SURFACE S= PP*	Final strenght	type of failure
polychloroprene adhesive in organic solvent blend	20-30	cohesion of adhesive
nitrile adhesive in organic solvent blend	20-30	cohesion of adhesive
vinyl adhesive in water dispersion	40-50	cohesion on wood surface
acrylic adhesive in water dispersion	40-50	cohesion on wood surface
cyano-acrylic liquid adhesive	50-60	wood cohesion
moisture-curing polyurethane liquid adhesive	50-60	wood cohesion
epoxy bicomponent liquid adhesive	60-80	wood cohesion

* wiped with methyl ethyl ketone

EXAMPLE 2: a chloroacetovinyl resin, e.g Vinylite VMCH (trademark of the UNION CARBIDE CHEMICALS) is dissolved in a blend of organic solvents preferably as follows:

PRIMER 2

VMCH	(trademark UNION CARBIDE CHEMICALS)	1,98
Toluene		9,17
methyl ethyl ketone		22,21
Nappar6	(trademark of EXXON)	66,50
TOTAL		100,00

Bond values Kg/cm obtained with PROCESS P.0 by using PRIMER 2 are shown in the following TABLE 2.

TABLE 2

SURFACE S	Initial strenght	type of failure	Final strenght	type of failure
PE LD *	8-10	Adhesion	15-17	adhes./cohes. on surface

* wiped con Nappar6 (EXXON trademark)

EXAMPLE 3: a chlorosulphonated polyethylene, e.g. Hypalon48 (trademark of DuPONT DOW ELASTOMERS), is dissolved in a blend of organic solvents preferably as follows:

PRIMER 3

Hypalon48 (DuPONT DOW ELASTOMERS trademark)	2,45
Methylmetacrylate	0,98
4-chlorobenzophenone	0,49
toluene	73,41
acetone	22,68
TOTAL	100,00

Bond values Kg/cm obtained with PROCESS P.0 by using PRIMER 3 are reported in the following TABLE 3.

TABLE 3

SURFACE S	Initial strenght	type of failure	Final strenght	type of failure
EVA expanded	1-2	adhesion	4-5	Adhesion
PP *	4-5	adhesion	8-12	adhes./cohes. on surface
PE LD *	8-10	adhesion	15-17	adhes./cohes. on surface

* wiped con Nappar6 (EXXON trademark)

EXAMPLE 4: a chlorinated polyethylene acid copolymer, e.g Hypalon 337 (trademark of DuPONT DOW ELASTOMERS) is dissolved in a blend of organic solvents preferably as follow:

PRIMER 4

Hypalon337 (DuPONT DOW ELASTOMERS trademark)	2,50
toluene	97,50
TOTAL	100,00

Bond values Kg/cm obtained with PROCESS P.0 by using PRIMER 4 are reported in the following TABLE 4.

TABLE 4

SURFACE S	Initial strenght	type of failure	Final strenght	type of failure
PE LD *	3-4	adhesion	10-15	ades./coes.superficiale

* wiped con Nappar6 (EXXON trademark)

EXAMPLE 5: Haloflex 208 (trademark of teh Firm ZENECA Resins) dispersion is diluted with water in order to obtain a dry content of about 2%, then wetting agents are added to improve the application, preferably as follows:

PRIMER 5

Haloflex 208 (ZENECA Resins trademark)	4,73
Carbopol E21 (BF Goodrich trademark)	0,39
water	93,09
NaOH 20%	0,74
Lutensit AFK (B.A.S.F. trademark)	1,05
TOTAL	100,00

Bond values Kg/cm obtained with PROCESS P.0 by using PRIMER 5 are shown in the following TABLE 5.

TABLE 5

SURFACE S	Initial strenght	type of failure	Final strenght	type of failure
PE LD *	adhesion	3-4	6-15	Adhesion

* wiped con Nappar6 (EXXON trademark)

EXAMPLE 6: a chlorinated natural rubber, e.g. Pergut S20 (Bayer AG trademark) and preferably having viscosity of 20 mPa.s at 20°C in toluene 20% and a phenolic resin are dissolved in a blend of organic solvents preferably as follows:

PRIMER 6

Pergut S20 (Bayer AG trademark)	1,10
Alresen PA 565 (HOECHST trademark)	1,22
methyl ethyl ketone	1,42
toluene	90,30
acetone	5,96
TOTAL	100,00

Bond values Kg/cm obtained with PROCESS P.0 by using PRIMER 6 are shown in the following TABLE 6.

TABLE 6

SURFACE S	Initial strenght	type of failure	Final strenght	type of failure
PP*	4-5	Adhesion	8-12	ades./coes.superficiale
PE LD *	1-2	Adhesion	15-17	Adhesion

* wiped con Nappar6 (EXXON trademark)

EXAMPLE 7: a polychloroprene water dispersion, e.g NPX 9368 (trademark of Du PONT DOW ELASTOMERS) , is diluted in order to obtain a dry content of about 2%, then wetting agents are added to improve the application, preferably as follows:

PRIMER 7

NPX 9368 (DuPONT DOW ELASTOMERS trademark)	2,50
Water	94,72
Carbopol E21 (BF Goodrich trademark)	0,35
NaOH 20 %	0,66
TOTAL	100,00

Bond values Kg/cm obtained with PROCESS P.0 by using PRIMER 7 are reported in the following TABLE 7.

TABLE 7

SURFACE S	Initial strenght	type of failure	Final strenght	type of failure
PE LD *	1-2	Adhesion	5-6	adhesion

*wiped con Nappar6 (trademark of EXXON)

Experimental data here reported evidence that the main advantage achieved by using this method consists of improving bond of plastic materials of the polyolefin family, omopolymers, copolymers, either thermoplastic o crosslinked, expanded or not expanded, alone or properly compounded with plasticizers, extender, fillers, organic or inorganic fibres, stabilizers, chemical additives, as for example ethylenevinylacetate, crosslinked or not crosslinked.

The use of this method for example in shoe manufacturing, allows to obtain very good bonds both onto polyolefin based soles, crosslinked or not, and onto ethylenevinylacetate based soles as well, crosslinked or not, reaching bond values close to cohesion values of materials and anyhow complying, with or depassing minimum requisites set by EN1391 standards.

CLAIMS

1) Method for bonding polyolefinic plastic materials, omopolymers, copolymers, either thermoplastic or crosslinked, expanded or not expanded, alone or properly compounded with plasticizers, extender, fillers, mineral or organic fibres, stabilizers, chemical additives, said method including:

- the application onto said polyolefin plastic material of a layer of a solution containing 0.5% up to 10 % of a chlorinated organic compound dissolved into an organic solvent blend in the ratio of 99.5% to 90 %;
- a first evaporation of solvents contained in said solution;
- the exposure to ultraviolet radiations of said material treated with said solution;
- the cooling of said material;
- the application of an adhesive, either organic solvent based or water based, with or without crosslinker, both onto the polyolefin plastic material and at least one other substrate to which said material has to be bonded, said application being followed by a second evaporation of said organic solvents or water contained in said adhesive, or the application of a melted not volatile adhesive both onto said polyolefin plastic material and said at least one other material to be bonded thereto:
- the coupling , applying pressure, of the treated surfaces of said materials.

2) Method according to claim 1 in which said application of said adhesive is followed by a heat reactivation of the treated surfaces of said materials to be bonded together.

3) Method according to claim 1 which includes, before the application of said solution, the cleaning of each surfaces to be bonded with solvents belonging to the family of ketone, or esters, or chlorinated, or aromatic and aliphatic hydrocarbons.

4) Method according to claim 1 in which the adhesive is based on polymers choosen from the group of polyurethane, polycloroprene, styrene-butadiene-styrene or styrene-isoprene-styrene block copolymers, styrene-butadiene rubber, nitrile rubber, acrylic resins, cyanoacrylate, vinyl resins, epoxy resins dissolved in a blend of organic solvents, or in water dispersion, or in a non volatile composition, with or without curing agent.

5) Method accordingg to claim 1 in which said chlorinated organic compound are choosen from chlorinated natural rubber, or vinylchloroacetate resins, or chloropolyolefine resins, or chlorovinylacrylic resins, or polychloroprene.

6) Method according to claim 5 in which said chlorinated organic compound also include phenolic resins.

7) Method according to claim 5 in which said chlorinated organic compounds constituted by said chloropolyolefine resins are based on chlorosulphonated polyethylene.

8) Method according to claim 1 in which said organic solvent blend contained in said solution of chlorinated organic compound is constituted of aromatic hydrocarbons, ketones, esters and their blends.

9) Method according to claim 8 in which said aromatic hydrocarbons are constituted by toluene, xylene and/or the like.

10) Method according to cliam 1 in which said solution of chlorinated organic compound is constituted by chlorinated natural rubber, toluene, methyl ethyl ketone, ethyl acetate ed acetone.

11) Method according to claim 1 in which said solution of chlorinated organic compound is constituted by chloroacetovinyl resin, toluene, methyl ethyl ketone and aliphatic hydrocarbons.

12) Method according to claim 1 in which said solution of chlorinated organic compound is constituted by chlorosulphonated polyethylene, methylmetacrylate, 4-chlorobenzophenone, toluene, acetone.

13) Method according to claim 1 in which solution of chlorinated organic compound is constituted by chlorinated polyethylene acid copolymer and toluene.

14) Method according to claim 1 in which said solution of chlorinated organic compound is constituted by chlorovinylacrylic copolymers, water, NaOH 20%, and thickener.

15) Method according to claim 1 in which said solution of chlorinated organic compound is constituted by chlorinated natural rubber, phenolic resin, methyl ethyl ketone, toluene ed acetone.

16) Method according to claim 1 in which said solution of chlorinated organic compound is constituted by polychloroprene, water, NaOH 20% and thickener.

17) Method according to claim 1 in which said first evaporation is carried out between 5 and 6 minutes.

18) Method according to claim 1 in which said exposure to ultraviolet radiations ranges from 5 up to 30 seconds depending on the condition in which the distance of the radiation source, having total power in the range 400 to 4000 Watt, from said polyolefinic surface can vary from 0.1 to 0.3 metres.

19) Method according to claim 1 in which said cooling is carried out in about 5 minutes.

20) Method according to claim 1 in which said heat reactivation is carried out at temperature ranging from 20°C to 80°C.

21) Use of a solution containing 0.5 up to 10 % of a chlorinated organic compound dissolved into an organic solvent blend in the ratio of 99.5 to 90 % as bonding element for polyolefinic plastic materials of the type omopolymers, copolymers, either thermoplastic or crosslinked, expanded or not expanded, alone or properly compounded with plasticizers, extender, fillers, mineral or organic fibres, stabilizers, chemical additives, with said polyolefinic plastic materials being mainly used and bonded as shoe components, like soles or midsoles, waterproofing or fluid-tight membranes, slabs for wall-paneling or for flooring, or insulating panels, or rigid or semirigid plastic structures, to themselves or to substrates of different nature like metal, concrete, plastics, ceramics; as fluid transport pipes.

22) Use according to claim 21 in which said chlorinated organic compounds are choosen from chlorinated natural rubber, vinylchloroacetate resins, or chloropolyolefine resins, or chlorovinylacrylic resins, or polychloroprene.

23) Use according to claim 1 in which said chlorinated organic compounds are mixed with phenolic resins.

24) Use according to claim 21 in which said clorinated organic compounds constituted by said chloropolyolefine resins are based on chlorosulphonated polyethylene.

25) Use according to claim 1 in which said organic solvent blend contained in said solution of a chlorinated organic compound is constituted on aromatic hydrocarbons, ketones, esters and blends thereof.

26) Use according to claim 25 in which said solvents are constituted by toluene, methyl ethyl ketone, ethyl acetate ed acetone.

27) Use accoding to claim 21 in which said solution of chlorinated organic compound is constituted by chlorinated natural rubber, toluene, methyl ethyl ketone, ethyl acetate ed acetone.

28) Use according to claim 21 in which said solution of chlorinated organic compound is constituted by chloroacetovinyl resin, toluene, methyl ethyl ketone and aliphatic hydrocarbons.

29) Use according to claim 21 in which said solution of chlorinated organic compound is constituted by chlorosulphonated polyethylene, methylmetacrylate, 4-chlorobenzophenone, toluene, acetone.

30) Use according to claim 21 in which said solution of chlorinated organic compound is constituted by chlorinated polyethylene acid copolymer and toluene.

31) Use according to claim 21 in which said solution of chlorinated organic compound is constituted by chlorovinylacrylic copolymers, water, NaOH 20%, and thickeners.

32) Use according to claim 21 in which said solution of a chlorinated organic compound is constituted by chlorinated natural rubber, phenolic resin, methyl ethyl ketone, toluene ed acetone.

33) Use according to claim 21 in which said solution of a chlorinated organic compound is constituted by polychloroprene, water, NaOH 20% and thickener.

INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/EP 97/04198

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J5/12 C09J5/02 //C08L23:02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J A43B C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 692 276 A (BOSTIK SA) 17 December 1993 see claims 1,2,4,5,8,10-13 see example ---	1,2,4,5, 7-9,11, 13,21, 22,24, 26,30
X	WO 88 05346 A (WORTHEN IND INC) 28 July 1988 see claims 1,3-6 see examples --- -/--	1,2,4,5, 8,9,21, 22,25,26

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 December 1997	14/01/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Niaounakis, M

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate. of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 8932 Derwent Publications Ltd., London, GB; Class A17, AN 89-232388 XP002051071 & JP 01 168 783 A (NOGAWA CHEMICAL KK) , 4 July 1989 see abstract	21-23, 25,26
A	DATABASE WPI Section Ch, Week 7608 Derwent Publications Ltd., London, GB; Class A18, AN 76-14119X XP002051072 & JP 51 002 741 A (BOSTIK JAPAN KK) , 10 January 1976 see abstract	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte Jonal Application No
PCT/EP 97/04198

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 8805346 A	28-07-88	US 4778724 A	18-10-88
		US 4859540 A	22-08-89
		AU 1295988 A	10-08-88
		JP 3504250 T	19-09-91